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ENERGETIC MATERIALS FROM CUBANE

**FINAL TECHNICAL REPORT
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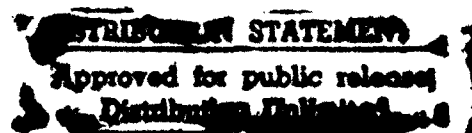
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Summary: New generations of highly energetic materials are required for the modern Navy. Cubane is a very dense, exceptionally energetic hydrocarbon; its heat of formation, density, and strain energy are all extraordinarily high -- in combination unexceeded by any other stable hydrocarbon. This dense, energetic system has 8 identical methine C-H groups at which hydrogen may be replaced by energy-rich substituents. The goal of this project is to understand the fundamental properties of the basic set of reactive intermediates that might be used for the functionalization of the cubane nucleus. Only cubane-1,4-dicarboxylic acid is available readily. Ways to introduce other substituents elsewhere on the cubane nucleus are needed. As cubanes are far from the ordinary in their chemical behavior, this necessitates the development of radically new methodology.

The enormous strain energy in the cubane system (+161 kcal/mole) makes cubanes very different chemically from ordinary compounds. New reactions have been invented, special reagents have been developed, and novel methods for functional group transformations have been found to provide for systematic elaboration of the cubane system.

In the course of this work we have characterized cubyl anion, cation (the least likely carbonium ion), and radical. We have developed methodology for using each of these as intermediates in the synthesis of new cubanes. We have worked out the chemistry of cubyl carbinyl systems, including the radical (the fastest rearranging alkyl radical), anion and cation. We have prepared cubene, the most pyramidalized olefin, and 1,9-homocubene, the most twisted olefin. We discovered 1,4-cubanedyl, a new kind of organic intermediate. We have prepared and started the characterization of a completely new kind of rigid rod polymer. We have developed amide-activated ortho-metalation technology for the functionalization of strained systems. We have applied this to practical synthesis of important aromatic compounds. We discovered ortho-magnesiumation, an environmental satisfactory method for metalation of aromatics. We have put the fundamental chemistry of the cubane system "on the map". It is now ready for inclusion into organic textbooks.

In the course of our ONR-sponsored work on the cubane system, there has been a rich fall-out applicable to non-ONR problems. This has permitted us to introduce new methodology for the synthesis of the important, heat-stable polyimide resins; to prepare polycubanes designed to be liquid ferroelectric crystal switches, to open the possibility of using cubanes to approach stabilized polyacetylene semiconductors, and to start work on the evaluation of substituted cubanes as antiviral agents. We have prepared many new cubanes. Forty-one of these have been submitted to the National Cancer Institute for screening against AIDS and various malignant tumors. To date, 11 compounds have shown interesting activity, sufficient to merit additional testing.

Technical Reports: Publications (copies attached) have been submitted in lieu of technical reports. A list follows:

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